TITLE   REMARKS ON SOLID STATE AMORPHIZING TRANSFORMATIONS

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REMARKS ON SOLID STATE AMORPHIZING TRANSFORMATIONS

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ABSTRACT

Amorphous solids can be now produced through a variety of laboratory synthesis techniques as well as through many naturally occurring processes. In general, we can classify the methods of synthesis of amorphous solids AS followS: (a) rapid solidification of melts or vapors; (b) atomic disordering of crystalline lattices; (c) solid state reactions between pure elements; (d) solid-state transformations from metastable crystalline states; and (e) deposition from electrolytes. We give a short summary of the historical development of methods (a)-(d) [method (e) is clearly outside the focus of this conference] and we discuss the basic physical principles behind the methods.

1. Synthesis of Amorphous Solids by Rapid Solidification

Ionic and covalent glasses often form when the corresponding melt fails to crystallize during relatively slow cooling, of the order of 1 K/s. Naturally occurring oxide glasses such as obsidian were the first known to man who as early as 70,000 BC used them to make tools. Around 5,000 BC the Phoenicians discovered oxide-glass making and near 300 BC they developed the "blowing iron" technique.

In contrast to oxide melts, metallic melts exhibit far less resistance to crystallization when undercooled and as a consequence do not form glasses at ordinary cooling rates. During the 1950's, Buckel and Hilsch [1] demonstrated that pure amorphous metals could be formed if a metallic vapor was quenched onto a cryogenically cooled substrate to impede the formation of crystallites. Beginning in 1960, Duwez and his colleagues [2] developed rapid melt quenching techniques and showed that certain metallic alloys melts can be solidified to the glassy state at cooling rates of 10^6 K/s and higher. These developments led to the recognition that an amorphous phase can form in nearly any material when suitable kinetic constraints are imposed during cooling of either the liquid and/or vapor phase of the material. For most molten metallic alloys the required cooling rate for avoiding crystallization is 10^6 K/s or higher and this limits one of the dimensions of the amorphous product to less than 30 μm. Recently, Drehman, Greer and Turnbull [3] showed that the observed small barrier to crystallization in undercooled metal melts arises primarily from the presence of foreign inclusions, such as oxide particles, which act as heterogeneous nucleation centers. By carefully removing these centers in molten $Pd_{40}Ni_{40}P_{20}$, the authors were able to prepare cm-size amorphous samples of this alloy at cooling rates of the order of 10^2 K/s. These experiments further confirmed the thermodynamic prediction that alloy melts with a large ratio between the glass transition temperature, T_g, and the melting temperature, T_m, should have a relatively high resistance to crystallization in the temperature regime T_g - T_m.

2. Synthesis of Amorphous Solids by Disordering the Crystalline Lattice

As for the previous class of synthesis methods, nature provided the first examples of amorphous solid formation by disordering the lattice of a stable crystalline solid. Observations of amorphous minerals date back to the work of the Danish mineralogist Broegger.[4] During the 1890's, he noted that certain naturally occurring and originally crystalline minerals such as gadolinite, thorite, and zircon, had in the course of geological times assumed the properties of an amorphous material. He attributed this transformation to the presence of "outside influences affecting the complicated molecules" and named the amorphous minerals "metamikte" from Greek for "mix otherwise" because of their complex compositions. In 1914, Hamberg [5] suggested that metamictization is a periodic-to-aperiodic phase transition induced by the lattice disordering resulting from the emission of alpha particles from radioactive decays. That such minerals were indeed amorphous was confirmed by the x-ray diffraction studies of Rinne [6] and Vegard [7]. It is now accepted that metamictization is caused by radiation damage to the crystal structure. During the past 15 years, irradiation induced amorphization using high-energy ion accelerators has been studied in detail in a wide variety of materials including metallic alloys and compounds.[8] In addition, crystal-to-amorphous transformations have been induced in the laboratory using neutron irradiation and electron irradiation in high-voltage electron microscopes.

The disordering of a crystalline lattice to form an amorphous alloy can also be accomplished by mechanical means. In 1981, Yermakov et. al.,[9] reported that the mechanical attrition of crystalline

intermetallic compounds of yttrium and cobalt led to the formation of an amorphous alloy powder. The amorphous state was confirmed by x-ray diffraction and Mössbauer measurements. This method has been demonstrated in a variety of alloys.

3. Synthesis of Amorphous Alloys by Solid State Reactions

In 1977, Malik and Wallace [10] reported the formation of amorphous $GdNi_2H_{4.35}$ by the absorption of hydrogen into crystalline $GdNi_2$. Yeh et al [11] studied the synthesis of amorphous $Zr_3RhH_{4.5}$ by the absorption of hydrogen into crystalline Zr_3Rh. These authors further showed that a large fraction of the hydrogen could be removed at low temperatures while retaining the amorphous structure of the metallic alloy. These examples showed that chemical energies can be used to drive a crystal-to-amorphous transformation in the solid state. The hydrogen atom, being small, can easily diffuse in crystalline intermatallics of large unit cells, allowing for the reaction to occur at temperatures below the crystallization temperature of the amorphous hydride. The chemical reaction certainly takes place at higher temperatures but then the product is a crystalline hydride.

The amorphization by solid state reactions is not limited to hydrogen diffusing into crystalline intermetallics. Hauser [12] and later Herd at al. [13] reported that metals can diffuse at low temperatures into amorphous semiconductors, such as tellurium, selenium and silicon, without causing the amorphous semiconductor to crystallize. The first example of two pure crystalline metals reacting to form a single-phase amorphous alloy was reported by Schwarz and Johnson [14]. . In this experiment, thin films of pure gold and lanthanum, a few tenths of a nm in thickness,

were fully reacted at 70 °C within a few hours. Two requirements were proposed for the solid state amorphizing reaction: (1) the two reacting metals must have a large negative heat of mixing and (2) the two metals must have vastly different diffusivities in each other and in the amorphous alloy to be formed. The first condition ensures that a thermodynamic driving force for the reaction exists. The second condition ensures that the amorphous alloy will form in preference to crystalline intermetallics, which have lower free energies. This kinetic selection of the reaction path is possible because one species diffusing in the other and in the amorphous alloy is sufficient for the solid state amorphizing reaction. On the other hand. the formation of intermetallics, which have crystalline structures quite different from those of the two starting metals, requires the atomic motion of both species. Thus, a "temperature window" opens for the solid state amorphizing reaction by choosing a pair of elements with vastly different diffusivities from each other while in the amorphous state.

Figure 1 illustrates the "temperature window" for the solid state amorphizing reaction showing the electrical resistance of a stack of altern.ting thin films of nickel and zirconium during the continuous heating from 300 to 1000 K, followed by a cooling to 300 K [15] From (a) to (b), the films do not interdiffuse and the resistance increases linearly with increasing temperature, which is expected for pure crystalline metals. At the temperature of (b), an amorphous alloy begins to form at the Ni/Zr interfaces. Because the resistivity of the amorphous alloy is larger than that of the pure nickel and zirconium used to form the alloy, the resistance of the multilayer film increases. The solid state amorphizing reaction ends at (c), when all the nickel and zirconium

have been consumed. From (c) to (d) the resistance is temperature independent and agrees with the usual observation that the resistivity of amorphous alloys is largely temperature independent. At (d) the amorphous alloy formed by the solid state amorphizing reaction begins to crystallize and the resistance decreases because the crystalline order introduced in the alloy allows for an easier electronic conduction. At point (e) the alloy has reached a thermodynamically stable state that is impervious to further temperature variations. The resistance of the crystalline alloy has a positive linear temperature dependence, as expected. The "temperature window" for the solid state amorphizing reaction is clearly that between points (b) and (d). In the present understanding of the solid state amorphizing reaction, point (b) denotes the onset of nickel diffusion (the smaller atom) in the amorphous alloy, while point (d) denotes the onset of zirconium diffusion (the larger atom) in the amorphous alloy.

A method particularly promising for the manufacture of homogeneous amorphous powders and in large quantities is based on the mechanical alloying (MA) of powders. MA is a high-energy ball milling technique that has been used extensively in industry to prepare dispersion-strengthened metal-based powders with controlled microstructures. In 1983 it was found [16,17] that the MA of a mixture of powders of two pure metals results in an amorphous alloy powder. The first mechanism proposed to explain the amorphization by MA was based on the rapid solidification of melt. It was thought that the localized plastic deformation (at the particle surfaces or at plastic shear bands) was sufficient to produce melt pools. These melts would solidify rapidly by heat conduction into the cooler (less deformed) regions of the particles. Calculations [18] showed that the

peak temperatures reached in the particles trapped between colliding balls are far below the melting temperature. It is presently believed that the amorphization during MA occurs through a mechanism similar to the solid state amorphizing reactions in thin films. After only about one hour of MA, the powder particles attain a finely layered structure formed by alternating films of the two starting elements which resembles that of the unalloyed thin films used in the solid state amorphizing reactions. Chemical diffusion at these boundaries is thought to be assisted by the point and lattice defects created by plastic deformation and by the momentary increase in the temperature of the particles trapped between colliding balls.

4. Solid State Transformations from Metastable Crystalline States

Recently, Blatter and Von Allmen claimed to have observed the polymorphic decomposition of a metastable solid solution of two metals formed under high temperature equilibrium conditions and subsequently thermally treated at relative low temperature.[19] The effect has been reported in several titanium and niobium based alloys with chromium, manganese, iron, cobalt and copper. These observations imply a reentrant melting behavior. Contrary to the solid state amorphizing reaction, this transformation neither involves a chemical reaction nor long-range diffusion. The transformation starts at grain boundaries and at the sample surface, suggesting a similarity to melting. Greer (this conference) has proposed that, in principle, the reaction is reversible, and occurs because the undercooled liquid has a large degree of chemical order.

The number of papers dealing with amorphization in the solid state

by these rather novel methods by now exceeds 100. It has become clear that these phenomena are rather ubiquitous.[20] The above cases of amorphization induced by high-energy particle irradiation, mechanically alloying, and chemical interdiffusion in gas/solid or solid/solid diffusion couples etc., are all examples of solid state transformations from the crystalline to the amorphous state and are thus named solid state amorphizing transformations. The products of these transformations are simply *amorphous alloys* while the amorphous phases formed from a parent liquid phase are termed *glasses*. A comparison of the atom pair radial distribution functions and thermal stabilities of amorphous and glassy $Ni_{40}Ti_{60}$ alloys [21] suggest that the two alloys are structurally similar. It is often presumed that this result is general and that amorphous alloys prepared by different techniques relax to a more or less common structure following thermal annealing at temperatures near the glass transition temperature. If this is true, then we can associate well defined thermodynamic and physical properties with an amorphous phase of specified composition. This assumption is in fact necessary if we are to understand solid state amorphizing transformations in terms of conventional thermodynamic potentials and driving forces. If in fact the amorphous phase can be viewed as an extension of the liquid phase through the glass transition, it then follows that solid state amorphizing transformations are closely related to ordinary melting.[20] We would expect to observe many of the features associated with melting such as preferential nucleation of the amorphous phase at surfaces, interfaces, boundaries, and defects. Further, we should expect to be able to extend our knowledge of melting by studying the evolution of a crystalline solid as it approaches a critical condition for vitrification and subsequently transforms to the

amorphous phase.

FIGURE CAPTION

Figure 1.   Electrical resistance of a multilayer system of Ni and Zr
films during the continuous heating and cooling at 10 K/min. The thermal
cycle has been repeated twice. During the second cycle the resistance
follows the line f-g traced during the cooling part of the first cycle.

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